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MATERIAL FOR PREVENTING THE ADHESION OF AQUATIC LIFE

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MATERIAL FOR PREVENTING THE ADHESION OF AQUATIC LIFE

[Suiseseibutsu no Fuchakuboushizai]

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[There are no amendments to this patent.]

Claims

1. A material for preventing adhesion of aquatic life, characterized in that a salt consisting of cation and anion dissolved in sea water is present as part of the paint component.
2. A material for preventing adhesion of aquatic life, characterized in that a salt consisting of cation and anion dissolved in sea water and another repellent are contained as part of the paint component.
3. The material for preventing the adhesion of aquatic life according to Claim 1 or 2, wherein said salt consisting of a cation and anion dissolved in sea water is sodium chloride.
4. The material for preventing the adhesion of aquatic life according to Claim 1 or 2, characterized in that said salt consisting of a cation and anion dissolved in sea water is potassium chloride.
5. The material for preventing the adhesion of aquatic life according to Claim 1 or 2, characterized in that said salt consisting of a cation and anion dissolved in sea water is magnesium sulfate.
6. The material for preventing the adhesion of aquatic life according to Claims 1, 2, 3, 4 or 5, characterized in that a [material] produced by coating said salt consisting of a cation and anion dissolved in sea water and/or repellent with an oil component is contained as part of the paint component.

Detailed Description of the Invention

[0001]

Object of the invention

Industrial application field

The present invention relates to a material for preventing the adhesion of aquatic life such as algae, barnacles and sea mussels to ship hulls, port facilities, fish preserves, and the like.

[0002]

Background of the Invention

Various types of seaweed, barnacles and sea mussels adhere to and inhabit ships and various types of port facilities, as well as fish preserves and other protective fish facilities, thereby compromising the durability and performance of these facilities. For this reason, paints

* [Numbers in the right margin indicate pagination of the original foreign text.]

have been developed that prevent the adhesion of aquatic life when applied to the hulls of ships. However, the aquatic life control effects resulting from these paints has not necessarily been adequate, and moreover, most of these paints contain tin compounds. Pollution of the surrounding ocean and contamination of sea life has been attributed to the elution and dispersion of these compounds.

[0003]

The inventors of the present invention, in light of this state of affairs, attempted to develop substances with superior adhesion prevention effects with respect to aquatic life, which also pose little threat of ocean contamination. Thus, countermeasures that have eventually resulted from attempts at basic research regarding the prevention of adhesion of these types of aquatic organisms include the use of antimicrobial effects inherent in substances that aquatic life avoids; the use of a repellent action by utilizing electrochemical properties of inorganic compounds; and the production of a material that resists adhesion via the reformation of the properties of surfaces to which marine life attempt to adhere. Investigations were thus carried out in regard to specific means whereby a clue might be had to a solution to these problems. Thus the results presented in Japanese Kokai Patent Application Nos. Hei 2[1990]-53867, Hei 2[1990]-53877, Hei 2[1990]-53878 and Hei 3[1990]-53879 may be cited.

[0004]

However, the inventors of the present invention continued their search for more common substances that can provide superior adhesion prevention effects relative to the substances disclosed in these publications, and continued their research based on the conjecture that a solution to these problems might be present in conditions that are directly related to the basic environment in which the aquatic life lives.

[0005]

Technological aspects to be developed

The present invention was developed as a result of this research, and attempts to develop a material for preventing the adhesion of aquatic life based on the idea that the physiological processes of aquatic life in sea water are maintained based on determinate levels of chemical substances dissolved in sea water. Consequently, if the levels of these chemical substances were

changed, then this would lead to the prevention of physiological processes, so that aquatic life would avoid this type of environment.

[0006]

Constitution of the Invention

Means to achieve the objective

Specifically, a substance that prevents the adhesion of aquatic life that is one of the inventions pertaining to this application is a substance that is characterized in that salt consisting of a cation and anion that is dissolved in sea water is contained as a paint component.

[0007]

In addition, the material for preventing adhesion of aquatic life that is the second invention pertaining to this application is characterized in that a salt consisting of a cation and anion that is dissolved in sea water and another repellent are contained as a paint component.

[0008]

In addition, the material for preventing the adhesion of aquatic life that constitutes the third invention pertaining to this application is characterized in that, in addition to the above conditions, the salt consisting of a cation and anion that is dissolved in sea water is sodium chloride.

[0009]

In addition, the material for preventing the adhesion of aquatic life that constitutes the fourth invention pertaining to this application is characterized in that, in addition to the above conditions, the salt consisting of a cation and anion that is dissolved in sea water is potassium chloride.

[0010]

In addition, the material for preventing the adhesion of aquatic that constitutes the fifth invention pertaining to this application is characterized in that, in addition to the above conditions, the salt consisting of a cation and anion that is dissolved in sea water is magnesium sulfate.

[0011]

In addition, the material for preventing the adhesion of aquatic life of the sixth invention pertaining to this application is characterized in that, in addition to the above conditions, a [material] produced by coating said repellent and/or salt consisting of a cation and anion that is dissolved in sea water with oil component is contained as a paint component.

[0012]

The present invention is described in additional detail below. First, a description will be presented regarding the salt consisting of cation and anion that is dissolved in sea water and is a characteristic constituent of the present invention. Sodium ions, magnesium ions, calcium ions, potassium ions and other cations, as well as chlorine ions, sulfate ions, hydrogen carbonate ions, bromine ions and other anions are dissolved in sea water, but it is salts formed from combinations of these cations and anions such as sodium chloride, potassium chloride and magnesium sulfate that are used in the present invention.

[0013]

In addition, examples of the repellent that can also be contained in the paint along with the salt include metals or compounds thereof such as copper and copper compounds that have lower toxicity relative to tin and tin compounds; eucalyptus oil (cinneols, eucalyptols) that have recently been discovered to have repellent effects; tannins, tannic acid, saponins, wasabi, red pepper (powdered extracts) and caffeine that have been shown to have a repellent effect due to their irritative or stimulatory actions; enzyme substances such as lipases, amylases and proteases that exhibit a repellent effect due to their action of breaking down proteins; nicotine, nicotinic acid and other poisons; aloe extract, propolis and other substance having wound healing action; sodium salicylate; limonene; barium titanate; amino-modified silicone oils; and tightly bound particles of zinc oxide, titanium oxide and water.

[0014]

Paints in which the above salts or repellents have been admixed may be used as paints having the same constitution as paints that are commonly used for preventing ship hull adhesion. Specifically, paints can be used that are produced by mixing, as necessary, appropriate ratios of resin components, extender pigments, colorant pigments, plasticizers, additives, and the like. Examples of resin components referred to herein include chlorinated rubbers, vinyl chloride,

vinyl chloride-vinyl propionate, chlorinated polyolefins, acrylic resins, styrene-butadiene, rosins, rosin esters, and rosin soaps. Examples of extender pigments include calcium carbonate, talc, quartz powder, barium sulfate and clay. Examples of colorant pigments include titanium white and red iron oxide, examples of plasticizers include dioctyl phthalate, tricresyl phosphate and paraffin chloride, and examples of additives include suspending agents, suspension inhibitors, leveling agents and the like. In addition, examples of solvent components include toluene, xylene, thinner and other organic solvents, but the material may also be free of solvent.

[0015]

A brief explanation is presented below regarding the methods for producing the adhesion prevention material of the present invention. For example, when sodium chloride is used as the salt comprising a cation and anion that is dissolved in seawater, the amount of sodium chloride is preferably about 100 parts with respect to 100 parts of resin, and mixing and preparation can be carried out by methods known in the art at ratios that may range from a few parts to hundreds of parts, thereby producing a material that contains sodium chloride as a component.

[0016]

In addition, an example of a method for producing an adhesion inhibitor material containing repellant in addition to sodium chloride will be discussed below. For example, when a material that is soluble is selected as the repellant, the repellant is mixed with a sodium chloride aqueous solution prepared beforehand, and the solution is then dried to produce a dry solid, whereupon this dry solid or material produced by binding this dry solid is mixed in the paint, thus producing the adhesion prevention material. A repellant auxiliary that enhances the aquatic life adhesion prevention effects of sodium chloride or manifest its own repellent effects together therewith may be used instead of repellant.

[0017]

In addition, in the above production method, the dry solid formed from the mixed aqueous solution of the water-soluble repellant together with sodium chloride or potassium chloride that is directly mixed with the paint may be immersed in silicone oil, as an example of the oil component, and may then be removed and dried before admixing and dispersing it in the paint. In this connection, adhesion prevention materials produced using this type of treatment are water repellant and smooth due to the action of the silicone oil that coats the sodium chloride or

dried solid. Consequently, for example, when this type of adhesion prevention material is painted onto ship hulls, this water repellent effect reduces the chance that sea water will come into contact with the sodium chloride and dried solid, thereby controlling elution of the sodium chloride or dried solid and extending the repellent effect of the adhesion prevention material. In addition, because the surface is smooth, an aquatic life adhesion prevention effect resulting from a mechanical action is present in addition to this repellent action possessed by the sodium chloride or dried solid. Of course, potassium chloride, magnesium sulfate, and the like may be used instead of sodium chloride in the above two manufacture methods, or these compounds may be used in mixtures of multiple types.

[0018]

Moreover, the adhesion preventing paint obtained by the above methods can be employed using well-known coating methods such as painting directly onto objects, or, alternatively, plates or sheets that have been coated with this paint may be affixed to objects. Moreover, this paint can be used in order to impregnate fibers, and these fibers can then be used for fish netting and the like.

[0019]

Operation of the invention

Paint containing salt consisting of cation and anion dissolved in sea water is applied to the hulls of boats and the like, and by this means, the concentration of these ions in the vicinity of the surface is increased relative to the ion concentration in ordinary sea water due to elution of the cations and anions by the sea water. As a result, adhesion of aquatic life to the hulls of boats and the like will not occur because an environment that is inhospitable with respect to the physiological processes of aquatic life is produced, although this effect is not necessarily clearly understood from a biological standpoint.

[0020]

In addition, when a repellent is also contained as coating component in addition to the above salts, a synergistic repellent effect is produced by the environmental repellent action of the ionized salt and the repellent action inherent in the repellent. Moreover, when a material produced by coating the above salt and/or repellent with oil is used as paint component, the water repellency or smoothness of the salt or repellent surface is improved, thereby improving

the persistence of the repellent effect and also producing an aquatic life adhesion prevention effect by means of a mechanical action.

[0021]

Application examples

Application examples are presented below. In Application Examples 1-5, sodium chloride was used as the salt consisting of a cation and anion that is dissolved in sea water, and only sodium chloride was admixed in the paint without another repellent. With Application Examples 6-9, on the other hand, sodium chloride was used as the salt consisting of a cation and anion that is dissolved in sea water, and repellents were admixed in addition to the sodium chloride in the paint. With Application Example 10 and Application Example 11, potassium chloride and magnesium sulfate alone were admixed in the paint as salts consisting of cations and anions that are dissolved in sea water. In Application Example 12, a material produced by coating sodium chloride with an oil component was admixed in the paint. Comparative Examples 1-3 were used as comparative examples for Application Examples 1-5 and Application Examples 8-11, and Comparative Examples 4 and 5 were used as comparative examples for Application Examples 6 and 7. Application Example 12 was used as a control for comparison with Application Example 1.

[0022]

The application examples and comparative examples are presented below.

Application Example 1

Sodium chloride was used as the salt consisting of a cation and anion that is dissolved in sea water. Specifically, sodium chloride manufactured by Japan Tobacco Industry (99% or greater sodium chloride) used as common commercially-available table salt was ground with a mortar and pestle. In addition, the paint was Acrylic A-198-XB acrylic resin manufactured by Dainippon Ink and Chemicals. This material already contained 1 part xylene as solvent with respect to 1 part of resin. 16 parts of the above milled table salt consisting of sodium chloride was stirred and mixed well with respect to 100 parts of Acrylic A-198-XB100 (resin 50 parts, xylene 50 parts) using a ball mill, thus producing the paint of Application Example 1 in which sodium chloride was a component of the paint.

[0023]

Application Example 2.

In the same manner as above, 25 parts of the above ground table salt used as sodium chloride was stirred and mixed well with 100 parts of Acrylic A-198-XB (50 parts resin, 50 parts xylene) using a ball mill, thus producing the paint of Application Example 2.

[0024]

Application Example 3

In the same manner as above, 50 parts of the above ground table salt consisting of sodium chloride was mixed and stirred with 100 parts of Acrylic A-198-XB (50 parts resin, 50 parts xylene) using a ball mill, thus producing the paint of Application Example 3.

[0025]

Application Example 4

In the same manner as above, 100 parts of the above milled table salt used as sodium chloride was stirred and mixed well with 100 parts of the above Acrylic A-198-XB (50 parts resin, 50 parts xylene) using a ball mill, thus producing the paint of Application Example 4.

[0026]

Application Example 5

The above Acrylic A-198-XB is a material that already contains xylene as solvent, but in this application example, xylene was added in consideration of casting of the paint during coating and mixing and adjustment time, and red iron oxide was also added as a colorant and thickener. 10 parts of the additional xylene, 50 parts of the above milled table salt used as sodium chloride and 10 parts of red iron oxide were stirred and mixed well with 100 parts (50 parts resin, 50 parts xylene) of Acrylic A-198-XB using a ball mill, thus preparing the paint of Application Example 5.

[0027]

Application Example 6

In addition, copper chloride ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) was prepared as water-soluble repellent in addition to the above sodium chloride, and saturated aqueous solutions of equivalent amounts were prepared using these as solutes. After mixing the two, the solution was filtered. The filtrate

as then heated to evaporate off the water and crystallize the material to produce a dry solid. This dry solid was then milled with a mortar and pestle to produce a powder. 16 parts of the above dried solid that had been ground was then stirred and mixed well with 100 parts of the above Acrylic A-198-XB (50 parts resin, 50 parts xylene) using a ball mill, thus producing the paint of Application Example 6 that contained dried solid produced from a mixed solution of sodium chloride and water-soluble repellent as one component of the paint.

[0028]

Application Example 7

With the exception that a commercially-available saponin reagent was used as the water-soluble repellent, a dried solid obtained in the same manner as in Application Example 6 was mixed and stirred in the same proportion as in Application Example 6 with 100 parts of Acrylic A-198-XB to prepare the paint of Application Example 7. Saponin is a glycoside that is widely distributed throughout the plant kingdom, and is the generic name of substances wherein the cyclized compounds are aglycons. Many of these compounds are amorphous powders, and also have hemolytic action, irritate the mucous membranes, cause lachrymation and are toxic to fish. These substances can be obtained from a wide variety of plants, and are generally nontoxic.

[0029]

Application Example 8

A material produced by mixing the above milled sodium chloride and eucalyptus oil reagent manufactured by Kanto Chemical was added and mixed at a ratio of 50 parts with respect to 100 parts of Acrylic A-198-XB (50 parts resin, 50 parts xylene), thus producing the paint of Application Example 8.

[0030]

Application Example 9

A milled product of the above sodium chloride was mixed at a ratio of 20 parts with respect to 80 parts of 5% catechol aqueous solution reagent produced by Kanto Chemical, and the material was powdered after drying. This material was then added and mixed at a ratio of 50 parts with respect to 100 parts of Acrylic A-198-XB (50 parts resin, 50 parts xylene), thus producing the paint of Application Example 9

[0031]

Application Example 10

Potassium chloride used as the salt consisting of a cation and anion that is dissolved in sea water was used, and, specifically, a material was used that was produced by using a mortar and pestle to grind potassium chloride reagent manufactured by Kanto Chemical. 50 parts of this ground potassium chloride was stirred and mixed well with 100 parts of the same Acrylic A-198-XB as above using a ball mill, thus producing the paint of Application Example 10.

[0032]

Application Example 11

Magnesium sulfate was used as the salt consisting of a cation and anion that is dissolved in sea water, and specifically, a material was used that was produced by using a mortar and pestle to grind magnesium sulfate reagent manufactured by Kanto chemical. 50 parts of this ground magnesium sulfate was stirred and mixed well with 100 parts of the same Acrylic A-198-XB as above using a ball mill, thus producing the paint of Application Example 11.

[0033]

Application Example 12

The sodium chloride of Application Example 1 was immersed in silicone oil SF8417 (amino-modified silicone oil) manufactured by Dow Corning Silicone, whereupon the material was removed and dried for 6 h in a heating furnace at 80°C. 50 parts of this dried oil-coated sodium chloride was stirred and mixed well with 100 parts of the same Acrylic A-198-XB as above using a ball mill, thus producing the paint of Application Example 12.

[0034]

Comparative Example 1

A paint produced by mixing powdered persimmon husk which was disclosed as an adhesion inhibitor paint in Japanese Kokai Patent Application No. Sho 53[1978]-102340 was mixed with the above Acrylic A-98-XB, and this material was used as the paint of Comparative Example 1.

[0035]

Comparative Example 2

Corn which is known to have repellent action with respect to aquatic life due to its irritant properties was mixed with the above acrylic A-198-XB, and this material was used as the paint of Comparative Example 2.

[0036]

Comparative Example 3

A material produced by mixing the same Acrylic A-198-XB not containing repellent component was used as the paint of Comparative Example 3.

[0037]

Comparative Example 4

With the exception that commercially-available tannic acid for reagent use was used as tannin water-soluble repellent, a dry solid obtained in the same manner as in Application Example 6 was stirred and blended in the same ratio as in Application Example 6 to prepare the paint of Comparative Example 4. Tannins are known to be responsible for the bitter flavor in persimmons and tea and are widely present in plants. They are generally named for their property of producing polyvalent phenolic acid as a result of hydrolysis, and are generally colorless and amorphous. Tannins also readily dissolve in water, have astringent properties and contain substances that render water-soluble proteins insoluble. Their pharmacological action has also been employed in antibacterial agents. Phloroglucinol and shibuol which contains gallic acid are known to be present in sour persimmons, and catechins are known to be present in teas.

[0038]

Comparative Example 5

In Comparative Example 5, the paint produced in Application Example 1 above was used as-is as the paint of Comparative Example 5.

[0039]

Next, a discussion of the testing methods used in order to confirm the adhesion prevention effects of the application examples will be presented. The plate test was carried out for Application Examples 1-5, Application Examples 8-12 and Comparative Examples 1-3, and

the beaker test and sea test were carried out as confirmation. In Application Examples 6 and 7 and Comparative Examples 4 and 5, substrate adhesion testing was carried out.

[0040]

The plate test involved applying a 5-cm circle of aquatic life adhesion preventing material M of the present invention onto an acrylic FRP substrate (1) with suitable dimensions as shown in Figure 1, and then affixing a purple mussel with a shell length of 3 cm at about the center thereof. The adhesion (implantation) location of the byssi of the purple mussel was then determined. Mussels and barnacles are aquatic organisms that are typically used in adhesion testing, and adhere readily to marine structures. These creatures were used in testing because the number of byssi can be counted in table tests, and objective data is readily obtained.

[0041]

The specific means whereby the purple mussel A is affixed involves directly affixing the mussel to the center of the material that is coated with the adhesion prevention material M, or affixing the mussel using instantaneous adhesive or the like via a rubbery plate with a thickness of about 1 or 2 mm, as in this test. The mussel is then placed in a sea water tank for 1 week, and the implantation behavior of the byssi is investigated. A condition in which byssi run across the adhesion prevention material M and extend to the acrylic FRP substrate (1) means that the byssi of the purple mussel are repelled by the adhesion prevention material M. A higher ratio (%) of byssi reaching outside the adhesion prevention material relative to the number of byssi that are generated indicates greater adhesion prevention effects. This type of test was carried out with a sample number of 2 in examples other than Application Examples 8 and 9, and a sample number of 3 was used in Application Examples 8 and 9 and in the comparative examples.

[0042]

In addition, the beaker test is carried out in order to increase the sensitivity of effect confirmation. This test method involves, as shown in Figure 2, coating the entire surface of a 300 cc beaker 2 with adhesion prevention material M, and after drying, filling the beaker with about 280 cc of water. The purple mussel A is then introduced and left therein for 1 week, and observations are carried out regarding whether the byssi from the purple mussel adhere (implant) on any of the beaker surfaces. A determination of adhesion prevention effects in this test is made based on death of the mussel or lack of byssi production, in which case a determination of

effective is made. A determination of no effect is made when byssi are generated and adhere to the bottom or side surfaces of the beaker, and the mussel is fixed thereto. Two beakers were prepared for each application example.

[0043]

The sea water test, plate test and beaker test are tests that are carried out in the laboratory, and so a test that is more realistic was carried out for Application Examples 5, 10 and 11. In this method, the adhesion preventing paint is applied to the hulls of fishing vessels, and the vessels are placed in sea water for 1 month, whereupon the seaweed adhesion is observed.

[0044]

In addition, the substrate adhesion test involved preparing vinyl chloride plates with dimensions of 10 cm x 35 cm x 3 mm, and then applying the above adhesion prevention material thereto. The vinyl chloride plates with applied adhesion prevention material were then affixed in an ordered arrangement on metal holders prepared separately, and weights were attached below the holders. Ropes were attached above, and all of the vinyl chloride plates were simultaneously immersed in sea water, and left affixed to a sea wall in a bay. After a determinate period of time, the plates were removed from the sea, and the adhesion condition of seaweed to the vinyl chloride plates was visually observed and investigated. This test was carried out using a sample number of 2, and was performed in the summer from July to August.

[0045]

Effect of the invention

Tables 1 and 2 present the results of the plate tests carried out in Application Examples 1-5 and Application Examples 8-12, as well as the results of Comparative Examples 1-3 used for comparison therewith. In addition, the results of the beaker tests carried out for the same examples are presented in Table 3. Table 4 presents the results of the substrate adhesion test carried out in Application Examples 6 and 7 and in Comparative Examples 4 and 5 used for comparison therewith.

[0046]

Table 1

プレート テスト	サンプル 1		サンプル 2	
実施例 1	23/23	100%	41/44	93%
実施例 2	足糸3本出すが、自分の殻に付着		足糸11本出すが自分の殻に付着	
実施例 3	足糸出さない		足糸4本出すが自分の殻に付着	
実施例 4	足糸2本出すが、自分の殻に付着		貝 死ぬ	
実施例 5	足糸出さない		足糸出さない	
実施例 10	足糸出さない		貝 死ぬ	
実施例 11	足糸出さない		足糸出さない	
実施例 12	足糸出さない		足糸出さない	
	サンプル 1	サンプル 2	サンプル 3	
実施例 8	足糸出さない	足糸出さない	足糸出さない	
実施例 9	足糸出さない	93/93 100%	58/58 100%	

Key: 1 Plate test
 2 Sample __
 3 Application Example __
 4 3 byssi produced, but adhered to own shell.
 5 11 byssi produced, but adhered to own shell.
 6 No byssi.
 7 4 byssi produced, but adhered to own shell.
 8 2 byssi produced, but adhered to own shell.
 9 Mussel died

* In the table, the denominators of the fractions denote the total number of implanted mussel byssi, and the numerators denote the number of byssi that implant by extending outside the coated surface of diameter 5 cm.

[0047]

Table 2

プレート テスト	サンプル 1	サンプル 2	サンプル 3
比較例 1	10/35 29%	12/41 29%	10/37 27%
比較例 2	13/58 22%	14/39 36%	16/47 4%
比較例 3	13/49 27%	13/45 29%	27/91 30%

Key: 1 Plate test
 2 Sample 1
 3 Sample 2
 4 Sample 3
 5 Comparative Example 1
 6 Comparative Example 2
 7 Comparative Example 3

* In the table, the denominators of the fractions denote the total number of implanted mussel byssi, and the numerators denote the number of byssi that implant by extending outside the coated surface of diameter 5 cm.

[0048]

Table 3

ビーカー テスト	サンプル 1	サンプル 2
実施例 1	足糸29本を出し側面に付着	足糸15本を出し底面に付着
実施例 2	足糸出さない	足糸出さない
実施例 3	足糸出さない	足糸出さない
実施例 4	貝 死ぬ	貝 死ぬ
実施例 5	貝 死ぬ	貝 死ぬ
実施例 8	貝 死ぬ	貝 死ぬ
実施例 9	貝 死ぬ	貝 死ぬ
実施例10	貝 死ぬ	貝 死ぬ
実施例11	貝 死ぬ	足糸出さない
実施例12	貝 死ぬ	貝 死ぬ

- Key:
- 1 Beaker test
 - 2 Sample 1
 - 3 Sample 2
 - 4 Application Example 1
 - 5 29 byssi produced and adhered to side surface
 - 6 15 byssi produced and adhered to bottom surface
 - 7 Application Example 2
 - 8 No byssi.
 - 9 Application Example 3
 - 10 Application Example 4
 - 11 Mussel died.
 - 12 Application Example 5

- 13 Application Example 8
- 14 Application Example 9
- 15 Application Example 10
- 16 Application Example 11
- 17 Application Example 12

[0049]

Table 4

基板付着 テスト	実施例 6	実施例 7	比較例 4	比較例 5
0 日	0 %	0 %	0 %	0 %
7 日	5 %	1 0 %	0 %	5 %
1 4 日	5 0 %	4 0 %	6 0 %	5 0 %
2 1 日	6 0 %	7 0 %	1 0 0 %	8 0 %
2 8 日	8 0 %	9 0 %	1 0 0 %	1 0 0 %

- Key:
- 1 Substrate adhesion test
 - 2 Application Example 6
 - 3 Application Example 7
 - 4 Comparative Example 4
 - 5 Comparative Example 5
 - 6 ___ days

[0050]

In the plate test, 23 of a total of 23 byssi extended outside the coated surface of diameter 5 cm in sample 1, and 41 of the total of 44 byssi extended outside this surface in sample 2, giving an average repellence of 97%. In Application Example 2, 3 byssi were generated in sample 1 and all of them adhered to the shell, whereas 11 byssi were generated in sample 2 and all adhered to the shell, giving a repellence of 100%.

[0051]

In Application Example 3, no byssi were generated in sample 1, and although 4 byssi were produced in sample 2, they all adhered to the shell, giving a repellence of 100%. In Application Example 4, 2 byssi were produced in sample 1 and all adhered to the shell, whereas the mussel died in sample 2, giving a repellence of 100%. Moreover, in Application Example 5, no byssi were produced in sample 1 or sample 2, giving a repellence of 100%. In Application Example 8, no byssi were produced in any of the samples. In Application Example 9, no byssi were produced in sample 1, and although byssi were produced in the other samples, they all extended outside the paint-coated surface, and the repellence was thus 100% in these application examples.

[0052]

In Application Example 10, no byssi were produced in sample 1, whereas the mussel died in sample 2, giving a repellence of 100%. In Application Example 11, no byssi were produced in sample 1 or sample 2, giving a repellence of 100%, and in Application Example 12, no byssi were produced in sample 1 or sample 2, giving a repellence of 100%.

[0053]

In contrast, in the material of Comparative Example 1 produced by mixing powdered persimmon husk disclosed in Japanese Kokai Patent Application No. Sho 53[1978]-102340 in paint gave an average of 28%. The material of Comparative Example 2 produced by blending corn in paint gave an average of 31%, and paint not containing antifoulant used for Comparative Example 3 (which actually employed Acrylic A-198-XB manufactured by Dainippon Ink and Chemical) gave an average of 28%. In light of these results, it was confirmed that the above application examples provided superior effects. In this connection, the two reagents cited as comparative examples are substances that are indicated in the literature or the like as having control effects.

[0054]

In addition to sodium chloride, repellent effects were also confirmed for other salts consisting of a cation and anion that is dissolved in sea water, as can be seen in the results of the plate tests of Application Examples 10 and 11.

[0055]

In addition, as indicated in the results of the plate test in Application Example 12, the material produced by coating sodium chloride with oil component had somewhat higher repellence effects relative to material not coated with oil component of Application Example 1, and it is predicted that improvement in the persistence of equivalent or better repellent effects will be produced.

[0056]

As is clear from the results of the beaker test presented in Table 3, in Application Example 1 of the present invention, 29 byssi were produced and adhered to the side walls of the beaker in sample 1 and 15 byssi were produced and adhered to the bottom of the beaker in sample 2. Thus, a determination of no effect was made. In Application Example 2, no byssi were produced in sample 1 or sample 2, and in Application Example 3, no byssi were produced in sample 1 or sample 2. A determination of effective was thus made for both application examples. In Application Example 5, the mussels died in sample 1 and sample 2, and thus a determination of effective was made. In Application Examples 8 and 9, the mussels died in all samples. /

[0057]

In addition, in Application Example 10 and Application Example 12, the mussels died in samples 1 and 2, and, in Application Example 11, the mussel died in sample 1, and no byssi were produced in sample 2. Based on these results, it was determined that repellent effects were present in both application examples.

[0058]

As in the plate test, it was confirmed in the beaker test, that repellent effects were present in all application examples with the exception of Application Example 1. In addition, there were clear differences in seaweed adhesion in the coated regions and uncoated regions for all paints in the ocean test carried out for Application Examples 5, 10 and 11, and thus adhesion prevention effects were confirmed in field testing as well.

[0059]

In Application Example 6 and Application Example 7 in which a repellent substance was included in addition to sodium chloride, there was no seaweed coating over the surface after a

period of about 1 month, and the surface was in comparatively good condition. In Comparative Example 4 and Comparative Example 5, on the other hand, 100% coverage was found. It was confirmed that Application Example 6 and Application Example 7 of the present invention had strong repellent effects relative to other adhesion prevention materials. In addition, both application examples were better than the comparative examples in regard to the condition of adhesion. In addition, the plate test and beaker test carried out for Application Examples 8 and 9 which contained additional repellent substance confirmed that repellent effects were present in paints having this type of constitution. Tannins and sodium chloride which were used in the comparative example have previously been confirmed by the inventors of the present invention as having adhesion prevention effects when used alone.

[0060]

The fact that sodium chloride, potassium chloride and other substances that are primary substances that constitute sea water have adhesion prevention effects is thought to be due to the production of conditions that disrupt the natural state of the environment. This action can also be seen, albeit conversely, in the natural world when fish pass by the mouths of rivers so that parasites will fall off where river water flows into the ocean.

[0061]

Thus, in cases where other repellents are used in conjunction, the repellent itself manifests adhesion prevention effects or manifests synergistic effects together with the action of salts such as sodium chloride. Alternatively, by adjusting the elution rate of salt such as sodium chloride, it may be possible to manifest an overall adhesion prevention effect that is not obtained using a salt such as sodium chloride or repellent alone.

[0062]

Furthermore, even when using traditional substances that provide adhesion prevention effects when used alone, the material must not lose its own adhesion prevention effects when it is dried from a mixed aqueous solution of sodium chloride or the like. In this connection, in Comparative Example 4, it is thought that the intrinsic adhesion prevention effects were lost as a result of a reaction between the sodium chloride and tannic acid or oxidation when the materials were heated during drying. However, with the catechol used in Application Example 9, which is a similar type of tannin, repellent effects were found. Consequently, repellents must be selected

that synergistically interact with the effects of the salt consisting of ions that are dissolved in sea water, such as sodium chloride.

[0063]

In addition, sodium chloride or the like that is dissolved in sea water is a pervasive substance, and even if it is eluted, the level of elution will be extremely small relative to the total dissolved amount because it is already present in large quantities in sea water. Consequently, its effects on sea life will be minimal and there will be no problems with environmental pollution. In addition, the material can be obtained extremely inexpensively, and can be manufactured at low cost. If the particle diameter of the salt such as sodium chloride or potassium chloride is large, then it will impede ship progress when used as a hull paint for vessels, and so it is preferable for the particle diameter to be small. In addition, it is desirable to carry out a surface treatment with a silane coupling agent, silicone oil, or the like, in order to improve the persistence of the effects and painted surface smoothness.

[0064]

Moreover, a material can be formed by allowing thread or sheet-form fiber to absorb an aqueous solution of salt such as sodium chloride or this sodium chloride together with water-soluble repellent, followed by drying the material and coating it with a common paint. It is important to note that the intent of the present invention relates to the disposition of the material so that the salt such as sodium chloride or this together with repellent can be eluted from the paint film of the paint.

[0065]

Moreover, a material can be formed by allowing thread- or sheet-form fiber to absorb a mixed aqueous solution of water-soluble repellent and sodium chloride, and then drying the material and applying a paint film thereupon using common paint, thereby including another repellent. It is important to note that the intent of the present invention relates to the disposition of the material so that the dried solid formed from a mixed aqueous solution of sodium chloride and water-soluble repellent can be eluted from the paint film of the paint. In addition, repellents are not restricted to those cited in the above application examples, and various types of repellents may be used.

Brief description of the figures

Figure 1 is a perspective view showing the plate test which is a test method for aquatic life adhesion preventing materials pertaining to the present invention.

Figure 2 is a perspective view showing a beaker test which is a test method used on the aquatic life adhesion preventing materials pertaining to the present invention.

- 1 Acrylic FRP substrate
- 2 Beaker
- A Purple mussel
- a Byssi
- M Adhesion preventing material

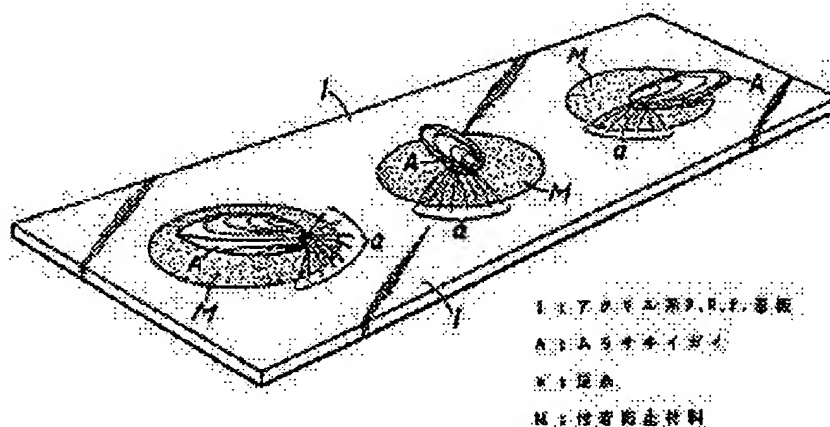


Figure 1

- Key:
- 1 Acrylic FRP substrate
 - A Purple mussel
 - a Byssi
 - M Adhesion preventing material

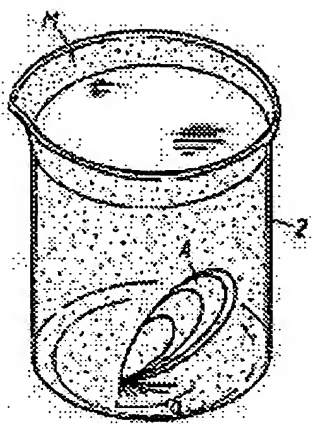


Figure 2